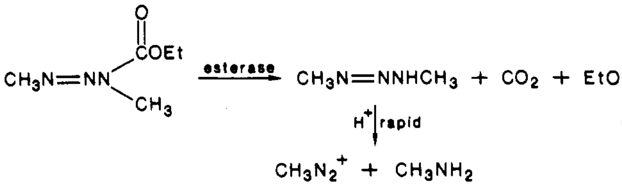
enhancing effect on the mutagenicity of DMC because it also contains nonspecific esterases. The esterase enhancement appears to be due to the liberation of 1,3-dimethyltriazene from DMC according eq 5.



(5)

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**Registry No.** DMT, 3585-32-8; DMA, 87031-64-9; DMC, 88211-12-5; DMP, 103711-39-3; DMM, 103711-40-6; diethyl *N*-methylphosphoramidate, 6326-73-4; ethyl *N*-methylcarbamate, 105-40-8.

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# Electrochemically Induced Aromatic Substitution. The 2-Nitropropane Anion, a Powerful Nucleophile in $S_{RN}1$ Aromatic Substitution

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In contrast with previous reports, the 2-nitropropane anion reacts readily with aryl radicals in the context of aromatic $S_{RN}1$ processes. This is shown in the examples of 4-bromobenzophenone and iodobenzene under electrochemical stimulation. The substitution products do not, however, result from the simple addition of the 2-nitropropyl anion on the aryl radical. The ensuing anion radical is indeed unstable, cleaving off a nitrite ion and thus leading to the cumene derivative as the main substitution product. Comparison of reactivity with diethyl phosphite and thiophenoxide ions shows that the 2-nitropropane anion is a quite powerful nucleophile in aromatic $S_{RN}1$ reactions.

$S_{RN}1$ aromatic substitution[2a] is a well-documented reaction.[2-4] To proceed, it requires the injection of electrons which can be provided photochemically,[2] or electrochemically[3] or by alkali metals dissolved in liquid ammonia[2] or by other redox reagents.[3b,c,f,h,4] As suspected from the effect of radical scavengers on the reaction[2b,g] and demonstrated on electrochemical grounds,[3] the reaction mechanism involves as starting step the transfer of an electron to the substrate, ArX, followed by the cleavage of the resulting anion radical $ArX^{\bullet-}$. The latter cleaves off the nucleofugal group $X^-$ (commonly a halide ion) giving rise to a σ-aryl radical which is the actual electrophile. This combines with the nucleophile, leading to the anion radical $ArNu^{\bullet-}$ of the substitution product. Removal of an electron from $ArNu^{\bullet-}$ yields the final substitution product ArNu. Reaction 4 represents the removal of the $ArNu^{\bullet-}$ odd electron by the same reactant, electrode, or redox reagent that served to inject an electron into ArX. Reaction 5 shows the possibility of a chain process when $ArNu^{\bullet-}$ transfers its odd electron to the substrate itself.

$$ArX + e^- \rightleftarrows ArX^{\bullet-} \qquad (1)$$

$$ArX^{\bullet-} \rightarrow Ar^{\bullet} + X^- \qquad (2)$$

$$Ar^{\bullet} + Nu^- \rightarrow ArNu^{\bullet-} \qquad (3)$$

$$ArNu^{\bullet-} - e^- \rightarrow ArNu \qquad (4)$$

$$ArNu^{\bullet-} + ArX \rightarrow ArNu + ArX^{\bullet-} \qquad (5)$$

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It has been shown[3] that the main side reactions, which function as termination steps in the chain process,[3b] consist of electron transfers to the easily reducible aryl radical (eq 6–8), Ar$^-$ being further trapped by the strongest proton

$$\mathrm{Ar}^{\bullet} + e^- \rightleftarrows \mathrm{Ar}^- \tag{6}$$

$$\mathrm{Ar}^{\bullet} + \mathrm{ArX}^{\bullet -} \rightarrow \mathrm{Ar}^- + \mathrm{ArX} \tag{7}$$

$$\mathrm{Ar}^{\bullet} + \mathrm{ArNu}^{\bullet -} \rightarrow \mathrm{Ar}^- + \mathrm{ArNu} \tag{8}$$

donor present in the reaction medium (eq 9), leading to ArH as side product besides the target compound, ArNu.

$$\mathrm{Ar}^- + \mathrm{H}^+ \rightarrow \mathrm{ArH} \tag{9}$$

This is what happens in poor H atom donor solvents such as liquid ammonia.[3a,f,h] In organic solvents, which are usually good H atom donors, an additional side reaction (termination step) is the abstraction of an hydrogen atom from the solvent by the aryl radicals which are excellent H atom scavengers[3d] (eq 10), thus leading the same side product ArH.

$$\mathrm{Ar}^{\bullet} + \mathrm{SH\ (solvent)} \rightarrow \mathrm{ArH} + \mathrm{S}^{\bullet} \tag{10}$$

A large number of nucleophiles have been shown to react in the $\mathrm{S_{RN}1}$ reaction: carbanions (including cyanide ions[3b,f,5]) and their silicon, germanium, and tin analogues, amide ions, anionic phosphorus, arsenic and antimony nucleophiles, and thiolates and their selenium and tellurium analogues.[6a]

Strangely enough, anions of nitroalkanes have acquired the reputation of being unreactive in $\mathrm{S_{RN}1}$ processes,[6] whereas they are typical nucleophiles in substitutions at certain aliphatic carbon sites.[7] We show hereafter that the 2-nitropropyl anion, a classical nucleophile in $\mathrm{S_{RN}1}$ aliphatic substitutions, does actually react in aromatic $\mathrm{S_{RN}1}$ processes. Two examples were investigated: reaction with 4-bromobenzophenone and iodobenzene under electrochemical stimulation in dimethyl sulfoxide (Me$_2$SO). It will be shown that carbon–carbon coupling does occur but that expulsion of NO$_2^-$ further takes place, the main product being then the CH(CH$_3$)$_2$-substituted compound. Comparison with benzenethiolate and diethyl phosphite ions, two classical nucleophiles in aromatic $\mathrm{S_{RN}1}$ reactions,[2,3] indicates that the 2-nitropropyl anion is a quite powerful nucleophile in these reactions.

## Results

**Cyclic Voltammetry.** In Me$_2$SO,[8a] as well as in other organic solvents such as dimethylformamide[8b] and acetonitrile,[8a] **4-bromobenzophenone** exhibits, at low sweep rates, an irreversible cathodic peak followed by the two waves, the first reversible and the second irreversible, of benzophenone (Figure 1a showing the two first waves of this system).

Upon addition of up to 0.1 M sodium or tetramethylammonium salts of 2-nitropropane no detectable modification of the cyclic voltammetric pattern occurs (Figure 1b).[9] The first wave of 4-bromobenzophenone becomes reversible upon raising the sweep rate and/or lowering the temperature.[8b] Addition of 2-nitropropane anions does not modify the cyclic voltammogram up to 2000 V s$^{-1}$ in Me$_2$SO at 20 °C or up to 200 V s$^{-1}$ in DMF at −40 °C. Similar results were also obtained with 4-chlorobenzophenone in DMF and acetonitrile.

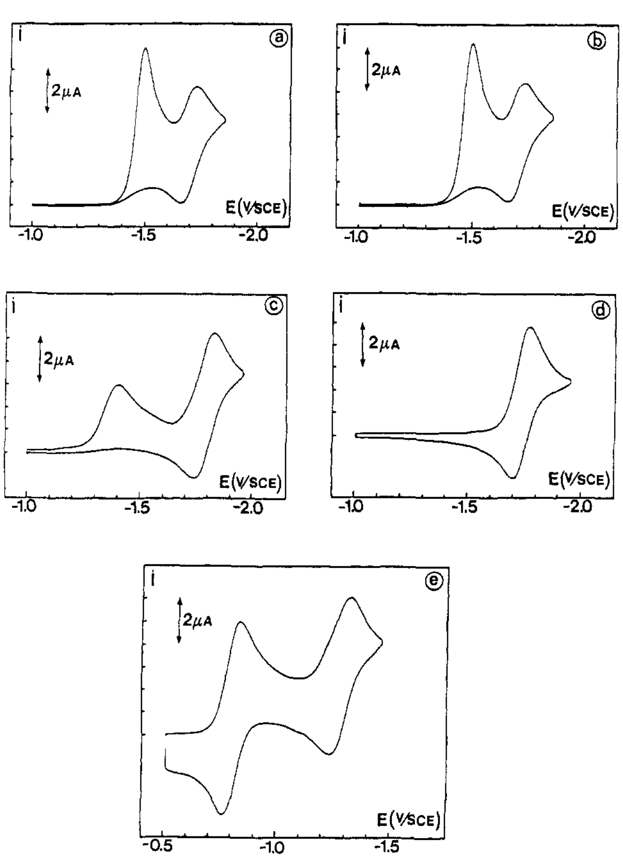

**Figure 1.** Cyclic voltammetry in Me$_2$SO + 0.1 M NBu$_4$BF$_4$ of (a) 4-bromobenzophenone (1 mM), (b) 4-bromobenzophenone (1mM) + tetramethylammonium 2-nitropropanate, (c) 4-benzoyl-$\alpha$-nitrocumene (1mM), 4-isopropylbenzophenone, and (e) 4-nitrobenzophenone: sweep rate; 0.2 V s$^{-1}$; temperature; 20 °C.

Figure 1 also shows the cyclic voltammetric behavior of three possible products of the reaction of 2-nitropropyl anions with the 4-benzoylphenyl radical, viz., 4-benzoyl-$\alpha$-nitrocumene (I), 4-isopropylbenzophenone (II), and 4-nitrobenzophenone (III).

I (Figure 1c) shows a first one-electron irreversible peak located −1.40 V vs. SCE (peak potential), i.e., positive to that of 4-bromobenzophenone [−1.50 V vs. SCE, at the same sweep rate (0.2 V s$^{-1}$)]. It is followed by a reversible one-electron wave ($E_\mathrm{p}$ = −1.82 V vs. SCE) and a further irreversible one-electron peak ($E_\mathrm{p}$ = −2.47 V vs. SCE). That cleavage of a nitrite anion occurs at the level of the first cathodic peak is attested by the fact that an anodic irreversible peak corresponding to oxidation of nitrite ions ($E_\mathrm{p}$ = +0.8 V vs. SCE) is observed, on a platinum electrode,

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(9) (a) With the exception in the case of the tetramethylammonium salt of a tensammetric[9b] peak located at −1.05 V. (b) I.e., a very narrow peak featuring the effect of the adsorption of the reactant on the double layer charging current. (c) Delahay, P.; *New Instrumental Methods in Electrochemistry*; Intersciences: New York, **1954**; p 144. (c) The observation of an oxidation wave of nitrite anions (possibly formed upon reaction of 4-benzoyl radicals with 2-nitropropane anions) in the far anodic region is made difficult by the oxidation of bromide ions (from the cleavage in the initial radical anion) in the same potential region.

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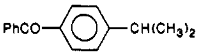
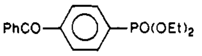
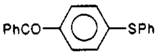
Table I. Electrolysis of 4-Bromobenzophenone[a] in $Me_2SO$ in the Presence of Nucleophiles[b]

| | | | products | | |
|---|---|---|---|---|---|
| nucleophile[c] | countercation[c] | electron/ molecule[d] | PhCOPh, % | $PhCOC_6H_4R$, %[d] | other, %[d] |
| $Me_2C^-NO_2$ | | | | $PhCOC_6H_4CH(CH_3)_2$ | |
| | $Na^+$, dibenzo-18-crown-6 | 2.0 | 26 | 50 | 4-benzoyl-$\alpha$-methylstyrene, 7 |
| | $NMe_4^+$ | 2.1 | 31 | 24 | |
| $OP(OEt)_2^-$ | | | | $PhCOC_6H_4P(O)(OEt)_2$ | |
| | $Na^+$, dibenzo-18-crown-6 | 1.5 | 42 | 10 | 4-methylbenzophenone, 10 |
| | $NMe_4^+$ | 2.2 | 51 | 8 | |
| $PhS^-$[e] | | | | $PhCOC_6H_4SPh$ | |
| | $Na^+$, dibenzo-18-crown-6[f,g] | 1.4 | 29 | 40 | |
| | $Na^+$ | 0.4 | 10 | 80 | |
| | $NBu_4^+$[f] | 0.3 | 0 | 60 | |

[a] Concentrations are 0.01 M unless otherwise stated. [b] At −1.5 V vs. SCE. [c] Concentrations are 0.1 M unless otherwise stated. [d] For each molecule of 4-bromobenzophenone consumed. [e] From ref 10. [f] 4-Bromobenzophenone concentration, $10^{-3}$ M. [g] $PhS^-$ concentration, 0.03 M.

Table II. Compared Reactivity of the Nucleophiles with the 4-Benzoylphenyl Radical[a]

| | substitution products, %[c] | | |
|---|---|---|---|
| nucleophiles[b] |  |  |  |
| $Me_2CNO_2,Na^+$ | 33 | 10 | |
| $OP(OEt)_2^-,Na^+$ | | | |
| $Me_2C^-NO_2^-,Na^+$ | 14 | | 30 |
| $PhS^-,Na^+$ | | | |
| $OP(OEt)_2^-,Na^+$ | | 8 | 34 |
| $PhS^-,Na^+$ | | | |

[a] In $Me_2SO$ + 0.1 M $NBu_4BF_4$, at 20 °C. Electrolysis potential, −1.5 V vs. SCE. 4-Bromobenzophenone concentration, $5 \times 10^{-3}$ $M^4$. [b] Concentration, $5 \times 10^{-2}$ M. [c] The percentages of substitution products correspond to one molecule of 4-bromobenzophenone consumed. The main side product was benzophenone.

upon scanning the potential over the first reduction peak of I.

The voltammogram of II (Figure 1d) is very closely similar to that of benzophenone itself. The first reversible one-electron peak is shifted cathodically by only 40 mV. It would therefore be practically impossible to detect the presence of II in a mixture of II and benzophenone by cyclic voltammetry.

III (Figure 1e) gives rise to two successive reversible waves ($E_p$ = −0.84, −1.32 V vs. SCE) even at low sweep rates. This shows that not only the corresponding anion radical is stable but also the dianion which is not surprising in view of the presence of two electron-withdrawing groups, PhCO and $NO_2$, in the conjugated system of the molecule.

If a reaction occurs upon reduction of 4-bromobenzophenone in the presence of 2-nitropropyl anion the above results show that III is not a product of the reaction: I, if formed, would not be stable since it is reduced irreversibly, with expulsion of a nitrite anion, at a potential positive to the reduction of 4-bromobenzophenone. In contrast, II may well be a product of the reaction since it cannot be distinguished from benzophenone on cyclic voltammetry grounds. If this happens it must however be emphasized that the overall process continues to involve the consumption of two-electrons per molecule as in the absence of 2-nitropropyl anion.

**Iodobenzene**, exhibits, in $Me_2SO$ at 20 °C, a single two-electron irreversible wave ($E_p$ = −1.89 V vs. SCE). No change is detected upon addition of 2-nitropropyl ions up to $10^{-2}$ M. Again, if reaction of the phenyl radical with the 2-nitropropyl anion occurred, leading to electroinactive products, like benzene itself, this would not alter the electron consumption.

**Preparative-Scale Electrolysis.** The cyclic voltammetry data do not permit one to distinguish between the absence of reaction and the possibility of a reaction not modifying the electron stoichiometry and leading to products that cannot be identified by their redox pattern. We therefore set up to investigate the products formed upon electrolysis at the reduction potential of the aryl halide.

Table I summarizes the results obtained with 4-bromobenzophenone, the main product is 4-isopropylbenzophenone. I and II were not found among the electrolysis products. Other products, in minor amounts, appear in the chromatographic analysis of the electrolyzed solutions. These were not systematically identified and quantitatively determined. Note, for example, the presence of a small quantity of 4-benzoyl-$\alpha$-methylstyrene.

Table I also contains the results obtained with diethyl phosphite and thiophenoxide ions as nucleophiles under similar conditions. Note in the case of diethyl phosphite ions, the presence of small amount of 4-methylbenzophenone is detected, which falls in line with the existence of a minor side reaction involving the dimsyl anion as a nucleophile.[8a] In order to measure the relative reactivities of the three nucleophiles, 2-nitropropyl anions, diethyl phosphite, and thiophenoxide ions, with the 4-benzoylphenyl radical we have reacted competively pairs of nucleophiles under the same electrochemical conditions. The results are listed in Table II. The reactivity of 2-nitropropyl anions was measured from the amount of 4-isopropylbenzophenone formed. This is only approximate since this is the major but not the only product resulting from the electrochemically induced reaction of 4-bromobenzophenone with 2-nitropropyl anions.

Similar experiments were carried out with iodobenzene as the substrate. The results are summarized in Tables III and IV. It is noticed that essentially two products benzene and a substitution product are found in the electrolyzed solutions. Since diethyl phosphite ions are practically unreactive (Table III) we carried out the competition experiments only with 2-nitropropyl and thiophenoxide anions (Table IV).

## Discussion

The results described above clearly demonstrate that 2-nitropropyl anions do react with aryl radicals, the initial

**Table III. Electrolysis of Iodobenzene[a] in $Me_2SO$ in the Presence of Nucleophiles[b]**

| nucleophile[c] | countercation[e] | electron/molecule[d] | products, %[d] | |
|---|---|---|---|---|
| | | | benzene | PhR |
| $Me_2C^-NO_2$ | | | | $PhCHMe_2$ |
| | $Na^+$, dibenzo-18-crown-6 | 2.0 | 96 | 4 |
| | $NMe_4^+$ | 2.0 | 71 | 29 |
| $OP(OEt)_2^-$ | | | | $PhP(O)(OEt)_2$ |
| | $Na^+$, dibenzo-18-crown-6 | 2.0 | 100 | 0 |
| | $NMe_4^+$ | 1.8 | 100 | 0 |
| $PhS^-$ | | | | PhSPh |
| | $NMe_4^+$ | 1.8 | 77 | 13 |

[a] Concentration, 0.01 M. [b] At −1.9 V vs. SCE. [c] Concentration, 0.1 M. [d] Per each reacted iodobenzene molecule. [e] Concentration, 0.1 M.

**Table IV. Compared Reactivity of 2-Nitropropyl and Thiophenoxide Ions with Phenyl Radicals**

| nucleophiles | products, % | | |
|---|---|---|---|
| | $PhCHMe_2$ | PhSPH | benzene |
| $Me_2C^-NO_2$,$NMe_4^+$<br>$PhS^-$,$NMe_4^+$ | 30 | 0 | 70 |

steps of the process being the same as in a standard $S_{RN}1$ reaction (eq 11–17). The primary substituted anion

$$ArX + e^- \rightleftarrows ArX^{\bullet -} \quad (11)$$

$$ArX^{\bullet -} \rightarrow Ar^\bullet + X^- \quad (12)$$

$$Ar^\bullet + Me_2C^-NO_2 \rightarrow ArC(Me)_2NO_2^{\bullet -} \quad (13)$$

$$ArC(Me_2)NO_2^{\bullet -} \rightarrow Ar\dot{C}Me_2 + NO_2^- \quad (14)$$

$$Ar\dot{C}Me_2 + e^- \rightleftarrows ArCMe_2^- \quad (15)$$

$$ArCMe_2^- + H^+ \text{ (solvent, residual } H_2O) \rightarrow ArCHMe_2 \quad (16)$$

$$H^+ + ArX + Me_2C^-NO_2 + 2e^- \rightarrow ArCHMe_2 + X^- + NO_2^- \quad (17)$$

radical, $ArC(Me_2)NO_2^{\bullet -}$, is, however, unstable as shown, in the case of 4-bromobenzophenone, by the fact that the first wave of $ArC(Me)_2NO_2$ is irreversible and involves the expulsion of one nitrite ion. The instability of the anion radicals of tertiary nitroalkanes has been observed previously in several cases.[11] Reduction of the resulting neutral alkyl radical yields the corresponding carbanion which rapidly protonates, leading ultimately to the cumyl-substituted product. Overall, the reaction thus consumes two electrons per molecule of starting compound. This is the reason why the reduction wave of the substrate was observed to undergo no change upon addition of 2-nitropropyl ions to the solution. The competitive formation of ArH results from the reduction of $Ar^\bullet$ at the electrode surface or in the solution or from H atom abstraction from the solvent as already discussed in the introduction.

In the above reaction schemes the reduction of the alkyl radical resulting from the loss of $NO_2^-$, $Ar\dot{C}Me_2$, is represented as occurring exclusively at the electrode surface. This is not in fact its only possible fate. It can also be reduced in the solution by electron transfer from $ArX^{\bullet -}$, abstract an H atom from the solvent, or undergo dimerization or H atom disproportionation. Note that the olefin which would result from the latter process has been found among the reaction products (Table I).

Iodobenzene and 4-bromobenzophenone offer two opposite examples as to the distance from the electrode at which the aryl radical $Ar^\bullet$ resulting from the decomposition of the initial anion radical $ArX^{\bullet -}$ starts to react (addition with the nucleophile, electron transfers, H atom transfer from the solvent). The anion radical of iodobenzene is extremely short-lived, with a life time of less than 1 ns.[12] It follows that the $ArC(Me)_2NO_2^{\bullet -}$ and $Ar\dot{C}Me_2$ radicals are formed very close to the electrode surface (90% of the $ArX^{\bullet -}$ anion radicals are destroyed within less, presumably much less, than 100 Å from the electrode surface). Among all the reactions that the $Ar\dot{C}Me_2$ radical may undergo, electron transfer from the electrode (eq 15) is the most likely. This explains why the substitution products essentially consist in the cumyl derivative in this case.[13]

The cleavage of the 4-bromobenzophenone anion radical is much slower ($k = 4 \times 10^4$ $s^{-1}$ [8]). Thus $Ar^\bullet$, $ArC(Me_2)NO_2^{\bullet -}$, and $Ar\dot{C}Me_2$ are formed far from the electrode surface (90% of the $ArX^{\bullet -}$ radicals are now destroyed within ~2000 Å from the electrode surface). $Ar\dot{C}Me_2$ is thus more likely to react in the solution than at the electrode surface. It still can be reduced by electron transfer, from $ArX^{\bullet -}$, leading to $ArC^-Me_2$ and ultimately to the cumyl derivative. However, it can, in addition, undergo other reactions such as dimerization and H atom transfer disproportionation. The olefin that would result from the latter reaction was actually found in the reaction products (Table I). At the same time $Ar^\bullet$ instead of being mostly reduced at the electrode surface may abstract hydrogen atoms from the solvent, yielding benzophenone and the dimsyl radical. The latter will then be further reduced into the dimsyl anion, which can react on the 4-benzoylphenyl radical along an $S_{RN}1$ reaction,[8a] yielding among other products the 4-methylbenzophenone, which was indeed found among the reaction products in the case where diethyl phosphite ions are used as nucleophile (Table I). It is thus not surprising that several products, besides the cumyl derivative and ArH, may be present in the case of 4-bromobenzophenone, whereas this is not the case with iodobenzene.

The obtention of substitution products resulting from the fragmentation of the anion radical obtained after the primary attack of the aryl radical by nucleophiles is not unprecedented. This has been shown to occur with carbanionic nucleophiles bearing a leaving group such as the dimsyl anion[8a] and the α-cyanoalkyl anions.[2b,f]

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(12) (a) It has been shown that the anion radicals of bromo and chlorobenzene have a lifetime smaller than a nanosecond in DMF.[12b,c] This is a fortiori true for iodobenzene since $I^-$ is a better leaving group than $Br^-$ and $Cl^-$ in the anion radicals of halo aromatics.[12d] (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (c) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 3806. (d) Andrieux, C. P.; Savéant, J. M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107.

(13) This also explains why poor substitution yields are obtained in the case of iodobenzene with all three nucleophiles under electrochemical stimulation. The opposite is true when the reaction is induced photochemically or by alkali metal dissolved in liquid ammonia as previously rationalized.[3b]

The strength of 2-nitropropyl anion in the aromatic $S_{RN}1$ reaction can be roughly estimated from the competition experiments summarized in Table II and IV. In the case of the phenyl radical, the 2-nitropropyl anion appears as more powerful than both thiophenoxide and diethyl phosphite ions. Toward 4-benzoylphenyl radical, its strength is in between that of diethyl phosphite and thiophenoxide ions. Note, however, that the reactivity of the 2-nitropropyl anion may be somewhat underestimated in this case since, among all the possible products resulting from the initial addition to the 4-benzoyphenyl radical, only the cumyl derivative was taken into account.

## Concluding Remarks

The main conclusions that emerge from the preceding results and discussion are as follows. 2-Nitropropyl anions and presumably the other nitroalkane anions do not deserve the bad reputation they have as to their reactivity toward aryl radicals in the context of the aromatic $S_{RN}1$ reactions. They actually react readily with aryl radicals, being more powerful than diethyl phosphite ions and comparable to thiophenoxide ions, two common nucleophiles in aromatic $S_{RN}1$ process. The substitution products do not, however, result from the simple addition of the nitroalkane anion to the aryl radical. The ensuing anion radical is unstable and cleaves off a nitrite ion, leading ultimately to, as the final product, the cumyl derivative, which is thus formed according to an overall two-electron per molecule stoichiometry. The reactions follows the same three first steps as an $S_{RN}1$ reaction: electron transfer to the substrate, cleavage of the resulting anion radical, giving rise to the aryl radical, and reaction of the nucleophile with the aryl radical. The ensuing steps are, however, different from the case of the chemical $S_{RN}1$ reaction: instead of being reoxidized at the electrode surface or by ArX in the solution (chain process), the anion radical resulting from the attachment of the nucleophile to the aryl radical cleaves off the nitrite ion and reacts further with an additional electron and a proton. The side reactions (electron transfer and/or H atom transfer to the aryl radical) are also the same as in the usual $S_{RN}1$ reactions.

## Experimental Section

**The electrochemical instrumentation** was the same as previously described.[10b] In cyclic voltammetry, the working electrode was mercury amalgamated on a gold disk with a 0.78-$mm^2$ surface area. In preparative-scale electrolysis it was a mercury pool with a 33-$cm^2$ area. In all cases the reference electrode was an aqueous saturated calomel electrode.

**Chemicals.** $Me_2SO$, from commercial origin, was purified by fractional crystallization before use. 4-bromobenzophenone, iodobenzene, 4-nitrobenzophenone, and dibenzo-18-crown-6 were from commercial origin and used as received. Authentic samples were prepared for identification of the other electrolysis products. 4-Isopropylbenzophenone was prepared by a Friedel–Crafts reaction;[14] diethyl (4-benzoylphenyl)phosphonate was prepared from 4-bromobenzophenone and triethyl phosphite in the presence of nickel chloride[15] [$Eb_{0.05}$ 204; 6 °C; NMR ($CDCl_3$) 7.2–8.2 (9 H, Ar protons), 4.0–4.5 (2 q, 4 H, $OCH_2$), 1.26 ppm (6 H, $OCH_2CH_3$)]; diethyl phenylphosphonate was prepared in the same manner; 4-benzoyl-$\alpha$-nitrocumene was prepared from 4-nitrobenzophenone and lithium 2-nitropropanoate in DMF.[16]

Tetramethylammonium diethyl phosphite, 2-nitropropanoate and thiophenoxide were prepared by mixing equimolar amounts of the corresponding acid with tetramethylammonium hydroxide in methanol or in acetonitrile. The resulting solution was then dried over magnesium sulfate and evaporated under vacuum. Tetramethylammonium 2-nitropropanoate was further purified by dissolution in methanol and precipitation with ether. The corresponding sodium salts were obtained by mixing equimolar amounts of sodium methoxide and the corresponding acid in methanol and evaporating the solution.

**Analysis of the Electrolysis Solutions.** The reaction products were identified by comparison (GLC, HPLC, mass spectrum) with authentic samples.

Benzene and cumene were determined by GPC over on a 2-m, 20% FFAP column. The derivatives of 4-bromobenzophenone were determined by liquid chromatography on a 25-cm, 4-mm RP18 Lichrosorb column eluted with water–methanol mixtures (60 mL/h) detection being by UV spectroscopy. On this column, benzophenone and diethyl (4-benzoylphenyl)phosphonate have the same retention time. Diethyl (4-benzoylphenyl)phosphonate was thus determined by HPLC on a Micropak $NH_2$ column (30 cm, 4 mm, 50:50 pentane–methylene chloride at 40 mL/h).

**Registry No.** $Me_2C^-NO_2 \cdot Na^+$, 24163-39-1; $Me_2C^-NO_2 \cdot NMe_4^+$, 69240-37-5; $OP(OEt)_2^- \cdot Na^+$, 2303-76-6; $OP(OEt)_2^- \cdot NMe_4^+$, 103384-70-9; $PhS^- \cdot Na^+$, 930-69-8; $PhS^- \cdot NBu_4^+$, 4670-62-6; PhCOPh, 119-61-9; $p$-$(CH_3)_2CHC_6H_4COPh$, 18864-76-1; $p$-$PhCOC_6H_4C(CH_3){=}CH_2$, 103384-71-0; $p$-$PhCOC_6H_4P(O)(OEt)_2$, 103384-72-1; $p$-$PhCOC_6H_4SPh$, 6317-78-8; PhSPh, 139-66-2; $PhS^- \cdot NMe_4^+$, 1559-67-7; $p$-$BrC_6H_4COPh$, 90-90-4; PhI, 591-50-4; $p$-$MeC_6H_4COPh$, 134-84-9; $C_6H_6$, 71-43-2; $PhCH(CH_3)_2$, 98-82-8; phenyl radical, 2396-01-2; 4-benzoylphenyl radical, 59922-54-2.

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